

# Vibrational Spectroscopic Studies on the Hofmann-Td-Type Clathrates: $M(\text{NH}_3)_2M'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (M=Mn or Cd and $M'=\text{Cd}$ or Hg)

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**Abstract.** IR spectra of  $\text{Mn}(\text{NH}_3)_2\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  (M=Cd or Hg), and IR and Raman spectra of  $\text{Cd}(\text{NH}_3)_2\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  (M=Cd or Hg) are reported. The spectral data suggest that the former two compounds are similar in structure to the latter two Td-type clathrates.

**Key words:** Hofmann-Td-type clathrate, inclusion compounds, ammonia, IR spectra, Raman spectra.

## 1. Introduction

The structures of  $\text{Cd}(\text{NH}_3)_2\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  and  $\text{Cd}(\text{NH}_3)_2\text{Hg}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  clathrate compounds have already been determined by single crystal X-ray diffraction methods; the former clathrate is monoclinic with the space group  $C2/c$  ( $C_{2h}^6$ ) [1], the latter being triclinic with the space group  $P\bar{1}$  ( $C_i$ ) [2]. In the host frameworks of these compounds, which are substantially isostructural, the  $M'$  ( $M'=\text{Cd}$  or Hg) atom is tetrahedrally coordinated to the carbon atoms of the four cyanide groups, while the cadmium atom is octahedrally surrounded by six nitrogen atoms, two are from the  $(\text{NH}_3)$  ligands attached to the Cd atom in position *trans* to each other, the other four are from cyanide groups. The  $M'(\text{CN})_4$  groups are linked by the  $\text{Cd}(\text{NH}_3)_2$  moieties to form a three-dimensional network. This structure provides two kinds of cavities ( $\alpha$  and  $\beta$ ) for the guest benzene molecules. The former approximates to a rectangular box, and the latter to a biprismatic cage, as has been illustrated in a number of papers [1–5]. This so-called Hofmann-Td-type host structure differs from that of the Hofmann-type clathrate, designated with a formula  $M(\text{NH}_3)_2M'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  (M=Mn, Fe, Co, Ni, Cu, Zn or Cd and  $M'=\text{Ni}$ , Pd, or Pt), in that in the latter M and  $M'$  exhibit octahedral and square planar coordination, respectively, while in the former the corresponding metals, M=Cd and  $M'=\text{Cd}$  or Hg, are octahedrally and tetrahedrally surrounded, respectively [1,2,5].

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Compounds possessing this type of host lattice reported to date have only been confined to those with a Cd atom in the octahedral arrangement [1–9]. Now, for the first time, we have replaced this Cd metal atom by Mn and prepared two new benzene clathrates with the formula  $\text{Mn(II)(NH}_3)_2\text{Cd(II)(CN)}_4 \cdot 2\text{C}_6\text{H}_6$  (denoted as Mn-Cd-Bz) and  $\text{Mn(II)(NH}_3)_2\text{Hg(II)(CN)}_4 \cdot 2\text{C}_6\text{H}_6$  (denoted as Mn-Hg-Bz). In this study we report the IR spectra of Mn-Cd-Bz and Mn-Hg-Bz (Raman spectra of these dark brown compounds could not be obtained by using the 488 nm or 515 nm line), and IR and Raman spectra of  $\text{Cd(NH}_3)_2\text{Cd(CN)}_4 \cdot 2\text{C}_6\text{H}_6$  (denoted by Cd-Cd-Bz) and  $\text{Cd(NH}_3)_2\text{Hg(CN)}_4 \cdot 2\text{C}_6\text{H}_6$  (denoted by Cd-Hg-Bz), of which the crystal structures are already known to be as Hofmann-Td-type clathrates [1,2]. For the purposes of comparison and discussion the host complex  $\text{Cd(NH}_3)_2\text{Cd(CN)}_4$  (denoted by Cd-Cd) has been prepared and its IR spectral data are also reported. It should be noted that several unsuccessful attempts have been made to synthesize the host complexes of the other clathrates studied.

## 2. Experimental

### 2.1. PREPARATIONS

All chemicals were reagent grade (Merck) and were used without further purification.

*Mn-M-Bz (M=Cd or Hg)*: 1 mmole  $\text{K}_2\text{M(CN)}_4$  solution in 20 mL water saturated with benzene was added to a solution containing 1 mmole of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and 2.2 mmoles of  $\text{NH}_3$ . After vigorous stirring for a day the brown precipitate (very fine powder) was filtered, washed with water, ethanol and ether, successively, and kept in a desiccator containing saturated benzene vapour and silica gel.

*Cd-Cd*: 2 mmoles of  $\text{Cd(CN)}_2$  solution in 20 mL of  $\text{NH}_3$  solution (25%) was left overnight in the open air. The plate like crystals formed on the top of the solution were filtered, washed with water, ethanol and ether, successively and kept in a desiccator containing  $\text{NH}_3$  vapour.

*Cd-Cd-Bz and Cd-Hg-Bz*: These compounds were prepared by the methods already described in References [1] and [2], respectively.

### 2.2. ANALYTICAL RESULTS

The freshly prepared samples were analyzed for Mn and Cd by a Philips PU9200 atomic absorption spectrophotometer, and for C, H and N by a Leco CHN-600 Model analyzer with the results as follows (found %/calculated %):  $\text{Mn(NH}_3)_2\text{Cd(CN)}_4 \cdot 2\text{C}_6\text{H}_6$ ; Mn: 11.85/11.90, Cd: 23.82/24.35, C: 44.40/43.50, H: 4.11/3.93, N: 16.83/17.30.

$\text{Mn}(\text{NH}_3)_2\text{Hg}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ; Mn: 10.35/9.99, C: 34.05/34.92, H: 3.05/3.33, N: 14.17/14.78.

### 2.3. SPECTRA

IR spectra of the freshly prepared compounds were recorded between  $4000\text{ cm}^{-1}$  and  $300\text{ cm}^{-1}$  on Perkin Elmer 1330 and 621 spectrometers, which were calibrated using a standard indene/camphor/cyclohexanone solution. The samples were prepared as mulls in nujol and hexachlorobutadiene in a CsI cell and as KBr discs. It should be noted that the compounds studied are found to partially decompose in the course of preparation (see below). The Raman spectra of the Cd-Cd-Bz and Cd-Hg-Bz compounds (in powder form) in a spinning cell were excited using a Spectra-Physics 2016-4S argon laser 514.5 nm line and recorded on a Jobin-Yvon U1000 spectrometer which was calibrated against the laser plasma lines.

## 3. Results and Discussion

The spectral features of the compounds under study are found to be similar to each other, suggesting that they also have similar structural features. These similarities in spectra, furthermore, suggest that the symmetry restrictions of the clathrate compounds with different crystal symmetry possibilities (at least Cd-Cd-Bz ( $P\bar{1}$ ) and Cd-Hg-Bz ( $C2/c$ )) are not effective. Therefore, the assignments were made by treating the benzene,  $\text{M}(\text{NH}_3)_2$  moieties and the  $\text{M}'(\text{CN})_4$  ions separately. The assignments and the wavenumbers of the observed bands arising from benzene,  $\text{M}(\text{NH}_3)_2$  and  $\text{M}'(\text{CN})_4$  moieties are tabulated in Tables I, II and III, respectively, together with some pertinent spectral data for comparison.

### 3.1. BENZENE VIBRATIONS

The assignments and the wavenumbers of the vibrational bands of benzene observed in the spectra of the clathrate compounds are listed in Table I, together with the frequencies of benzene in the liquid phase [10] and in the clathrates Cd(pyrazine)Cd(CN)<sub>4</sub> · 2C<sub>6</sub>H<sub>6</sub> [6] and Cd(NH<sub>3</sub>)<sub>2</sub>Ni(CN)<sub>4</sub> · 2C<sub>6</sub>H<sub>6</sub> [11, 12] on which the assignments are based.

The vibrational spectra of the benzene as a guest molecule have been reported for a number of Hofmann-type [11, 13–18] and Td-type [3, 6, 7] clathrate compounds. In these and in our spectra the spectral features are almost the same with the exception of the out-of-plane CH bending ( $A_{2u}$ ) vibration. This vibrational mode appears as a single band in the IR spectra of  $\text{M}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  (M=Mn, Fe, Ni, Cu, Zn and Cd) [13] and  $\text{Cd}(4,4'\text{-bipyridyl})\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  (M'=Cd or Hg) [7], while it splits into a doublet for  $\text{Cd}(\text{pyrazine})\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  (M'=Cd or Hg) [6] and a triplet for  $\text{Cd}(\text{ethylenediamine})\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  (M'=Cd or Hg) [3]. In the case of clathrates with a single band, because of the larger cavities due to the ligands, the interactions of the guest molecule with its surroundings are expected

TABLE I

The vibrational wavenumbers ( $\text{cm}^{-1}$ ) of  $\text{C}_6\text{H}_6$  in Mn-Cd-Bz, Mn-Hg-Bz, Cd-Cd-Bz, Cd-Hg-Bz and related compounds.

Assignment <sup>a</sup>	Liquid Benzene <sup>b</sup>		Cd-Cd-pyz-Bz <sup>c</sup>		Cd-Ni-Bz <sup>d</sup>		Mn-Cd-Bz		Mn-Hg-Bz		Cd-Cd-Bz		Cd-Hg-Bz	
	IR	Ra	IR	Ra	IR <sup>e</sup>	Ra <sup>f</sup>	IR	Ra	IR	Ra	IR	Ra	IR	Ra
$\nu_8 + \nu_{19}$	3075	-	-	-	-	-	3060w	-	3058w	-	3064m	-	3062w	-
$\nu_{20}E_{1u}$	3073	-	3088s	-	3076	-	3080w	-	3080m	-	3080m	-	3076m	-
$\nu_{13}B_{1u}$	3062 <sup>g</sup>	-	3068m	-	3026	-	3028m	-	3026m	-	3028s	-	3024m	-
$\nu_2A_{1g}$	-	3059	-	3062m	-	3064	-	-	-	-	-	3060m	-	3061m
$\nu_7E_{2g}$	-	3046	-	3057sh	-	3049	-	-	-	-	-	3040w	-	3040w
$\nu_5 + \nu_{17}E_{1u}$	1955	-	1951w	-	-	-	1968vw	-	1969w	-	-	-	1966w	-
$\nu_{10} + \nu_{17}$	1815	-	-	-	-	-	1824w	-	1824w	-	-	-	1823vw	-
$\nu_8E_{2g}$	-	1596	-	1586m	-	1583	-	-	-	-	-	1580w	-	1581m
$\nu_{19}E_{1u}$	1479	-	1479m	-	1476	-	1479s	-	1478s	-	1477m	-	1480s	-
$\nu_{14}B_{2u}$	1309	-	-	-	1311	-	1035vw	-	1302vw	-	-	-	-	-
$\nu_9E_{2g}$	-	1178	-	1177m	-	1178	-	-	-	-	-	1174m	-	1174m
$\nu_{15}B_{2u}$	1149	-	1147sh	-	1147	-	1145sh	-	1146sh	-	1145sh	-	1145sh	-
$\nu_{18}E_{1u}$	1036	-	1035m	-	1034	-	1033m	-	1032m	-	1032w	-	1035m	-
$\nu_{11}A_{1g}$	-	992	-	991vs	-	991	-	-	-	-	-	989vs	-	987vs
$\nu_{10}E_{1g}$	-	849	-	855w	-	869	-	-	-	-	-	854w	-	855w
$\nu_{11}A_{2u}$	670	-	685vs	-	704	-	698s	-	700vs	-	698s	-	701s	-
-	-	-	681vs	-	-	-	687vs	-	688vs	-	686vs	-	688vs	-
$\nu_6E_{2g}$	-	606	-	608m	-	608	-	-	-	-	-	604m	-	605m

<sup>a</sup> Using the numbering system of E.B. Wilson: *Phys. Rev.* **45**, 706 (1934).<sup>b</sup> Taken from ref. [12].<sup>c</sup> Cd(pyrazine)Cd(CN)<sub>4</sub>·C<sub>6</sub>H<sub>6</sub> [6].<sup>d</sup> Cd(NH<sub>3</sub>)<sub>2</sub>Ni(CN)<sub>4</sub>·C<sub>6</sub>H<sub>6</sub>.<sup>e,f</sup> Taken from refs. [16, 11], respectively.<sup>g</sup> Calculated value.

v=very, s=strong, m=medium, w=weak, sh=shoulder.

TABLE II

The vibrational wavenumbers ( $\text{cm}^{-1}$ ) of  $\text{NH}_3$  for Mn-Cd-Bz, Mn-Hg-Bz, Cd-Cd-Bz, Cd-Hg-Bz Cd-Cd and related compounds.

Assignment	Ni-Pd-Bz <sup>a</sup>		Cd-Ni-Bz <sup>b</sup>		Cd-Cd		Mn-Cd-Bz		Mn-Hg-Bz		Cd-Cd-Bz		Cd-Hg-Bz	
	IR	Ra	IR <sup>c</sup>	Ra <sup>d</sup>	IR	Ra	IR	Ra	IR	Ra	IR	Ra	IR	Ra
$\nu_a$ (IR)	3390m	-	3400s	-	3390s	-	3378s	-	3376s	-	3385g	-	3383s	-
$\nu_a$ (Ra)	-	-	-	3370	-	-	-	-	-	-	-	3370vw	-	3370vw
$\nu_s$ (Ra)	-	3284m	-	3294w	-	-	-	-	-	-	-	3290m	-	3291m
$\nu_s$ (IR)	3280m	-	3288s	-	3298s	-	3285m	-	3283m	-	3290s	-	3287s	-
$\delta_a$ (Ra)	1603m	1602m	-	1604	-	-	-	-	-	-	-	1600m	-	1601m
$\delta_a$ (IR)	1567	-	1562	-	1604m	-	1582m	-	1586m	-	1604m	-	1587m	-
$\delta_s$ (Ra)	-	1194	-	1153w	-	-	-	-	-	-	-	1190m	-	1192m
$\delta_s$ (IR) <sup>e</sup>	1160	-	-	-	-	-	1153w	-	1158w	-	1154w	-	-	-
$\delta_s$ (IR)	-	-	1109vs	-	1154vs	-	1126vs	-	1130vs	-	1109vs	-	1108vs	-
$\delta_t$ (IR)	604vs	-	542s	-	548vs	-	512s	-	513s	-	530vs	-	528vs	-
$\delta_t$ (Ra)	495vw	499m	-	513s	502m	-	-	-	-	-	-	505m	-	500m

<sup>a</sup>  $\text{Ni}(\text{NH}_3)_2\text{Pd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  [18].

<sup>b</sup>  $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ .

<sup>c,d</sup> Taken from refs. [13, 11], respectively.

<sup>e</sup> Band due to decomposed lattices.

v=very, s=strong, m=medium, w=weak, sh=shoulder.

TABLE III

Cyanide group vibrational wavenumbers ( $\text{cm}^{-1}$ ) for Mn-Cd-Bz, Mn-Hg-Bz, Cd-Cd-Bz, Cd-Hg-Bz, Cd-Cd and related compounds.

Symmetry and Assignment	$\text{K}_2\text{Cd}(\text{CN})_4^a$		$\text{K}_2\text{Hg}(\text{CN})_4^a$		Cd-Cd		Mn-Cd-en-Bz		Mn-Hg-en-Bz		Cd-Cd-en-Bz		Cd-Hg-en-Bz	
	IR	Ra	IR	Ra	IR	Ra	IR	Ra	IR	Ra	IR	Ra	IR	Ra
$\nu_1(\text{CN})\text{A}_1$	-	2149	-	2149	-	-	-	-	-	-	-	2178vs	-	2178vs
$\nu_2(\text{CN})\text{F}_2$	2145	-	2146	-	2168vs	-	2170vs	-	2167vs	-	2165vs	2165m	2168vs	2167m
Hot band?	-	-	-	-	2154vw	-	2157vw	-	2154vw	-	2154vw	-	2155vw	-
$\nu_3(^{13}\text{CN})$	-	-	-	-	-	-	2133vw	-	2132vw	-	2135vw	-	2136w	-
$\nu_2(\text{MC})\text{A}_1$	-	327	-	-	-	-	-	-	-	-	-	341vw	-	341vw
$\nu_6 + \nu_7$	-	-	-	-	600w	-	610m	-	612m	-	610w	-	608w	-
$\nu_6[\nu(\text{MC})+\delta(\text{NCM})]\text{F}_2$	316	-	330	-	357s,br	-	360s	-	368s	-	360s	-	358s	-

<sup>a</sup> Taken from ref. [29].

v=very, s=strong, w=weak, m=medium, sh=shoulder, br=broad.

not to be effective for splitting [7]. In the case of clathrates with doublet or triplet features the splittings have been ascribed to crystal field effects (strong host–guest interactions) [6]. In the IR spectra of our clathrates the CH out-of-plane mode appears as a doublet or triplet depending on the way of mulling: an IR spectrum of a clathrate obtained by mulling a small amount of crystalline sample in a mortar with a small amount of Nujol to yield a paste which is then transferred to a cell exhibits triplet splitting. On the other hand, a spectrum of a clathrate prepared by adding a drop of Nujol to a finely ground sample to yield a paste which is then transferred to a cell exhibits only doublet features. It is quite clear that some benzene is liberated from the clathrate on grinding; in the former preparation, liberated benzene dissolves in Nujol, giving one of the components of the triplet; in the latter preparation, the liberated benzene escapes and the band in question appears as a doublet. Therefore, we may reasonably suggest that of the three components of the triplet, which appear, for example, at 676, 688 and 698  $\text{cm}^{-1}$  for Cd-Hg-Bz, the band at 676  $\text{cm}^{-1}$  may be ascribed to the benzene dissolved in Nujol, since the CH out-of-plane bending mode of benzene in solution in a number of inert solvents appears at ca. 675  $\text{cm}^{-1}$  [19]. The bands at 698 and 688  $\text{cm}^{-1}$  may be assigned to two benzene molecules, the one in the  $\alpha$ -cavity and the other in the  $\beta$ -cavity. This suggests different interactions in each cavity. The possible interaction may be a weak hydrogen bonding between the ammonia molecules and the  $\pi$  electrons of the benzene ring as has been suggested for Hofmann-type [11, 13, 16, 17] and Td-type clathrates [6]. Accordingly, it is reasonable to suggest that the frequency shift of the out-of-plane CH mode ( $\nu_{11}$ ,  $A_{2u}$ ) and the consequential splitting may be explained by the differences in the strength of the hydrogen bonding between the ammonia molecules and the benzene molecules in different cavities. These spectral features may be explained by “*the concept of orbital following during molecular vibration*” [20–24]: The depletion of  $\pi$ -electron density of the benzene molecule by an electrophilic agent leads to a decreased ability of the carbon bonding orbitals ( $sp^2$ ) to follow the out-of-plane movement of the hydrogen atoms. This results in a higher bending vibration frequency, because the vibrations occur with greater difficulty as orbital overlap ( $sp^2$ - $\pi$ ) decreases. The same was stated for other member of Td-type compounds [7].

### 3.2. AMMONIA LIGAND VIBRATIONS

It has been found that the assignments of the vibrational bands of the ammine ligands in the IR and Raman spectra of the Hofmann-type clathrates and our compounds are consistent with the vibrational unit of  $\text{H}_3\text{N}-\text{M}-\text{NH}_3$  ( $D_{3d}$ ), in which the N–M–N skeleton is linear and the  $\text{NH}_3$  moieties are staggered [11, 13, 17]. Based on this model we expect two components, in-phase (Raman active) and out-of-phase (IR active) for each mode of a bare ammonia molecule. The assignment and the wavenumbers of the bands attributable to the ammine in the spectra of the compound under study are tabulated in Table II. For the purposes

of comparison and discussion, Table II also lists the wavenumbers of the IR and Raman spectra of the ammine ligands in some Hofmann-type clathrates [11, 13, 17], on which the assignments are based.

It is well known that Hofmann-type and analogous clathrates are unstable under ambient conditions and sensitive to grinding; even on mild grinding they decompose [11, 13, 16–18, 25–28]. In our case, although the Nujol mull preparations of the compounds were done with minimum grinding, IR spectra exhibit bands attributable to  $\text{NH}_3$  ligands in partially decomposed lattices (residual host lattice). These bands have readily been identified by making a comparison between the IR spectra of several Nujol mulls of clathrate obtained with different extents of grinding and the Cd-Cd host complex, since the IR spectrum of Cd-Cd shows a very strong band at  $1154\text{ cm}^{-1}$  due to the  $\delta_s$  vibration (Table II) while the corresponding band of the Cd-Cd-Bz clathrate appears at  $1109\text{ cm}^{-1}$ . These observations show that comparison of the bands at  $1109\text{ cm}^{-1}$  and  $1154\text{ cm}^{-1}$  can be used as a probe to appraise the extent of decomposition, since with gradual liberation of benzene the band at  $1109\text{ cm}^{-1}$  decreases in intensity, while the weak band at  $1154\text{ cm}^{-1}$  increases in intensity. A similar observation has been noted for Hofmann-type clathrates [13, 16]. The most striking spectral feature in the spectra of the clathrates are the considerable difference between in-phase (Raman active) and out-of-phase (IR active)  $\delta(\text{NH}_3)$  vibrations. It is still not quite clear to what extent the higher frequencies in the Raman compared to the IR arise from vibrational coupling through the metal or through an interaction via the benzene molecules [11, 13, 17]. However, Davies *et al.* suggested that the dominant cause is due to the hydrogen bonding interaction with benzene; since the metal M is a heavy atom, vibrational coupling through this atom should be rather weak and the  $\delta_s$  mode is strongly affected by a hydrogen bonding interaction with benzene [11].

### 3.3. $\text{Cd}(\text{CN})_4$ AND $\text{Hg}(\text{CN})_4$ GROUP VIBRATIONS

In assigning the bands attributable to the  $\text{M}'(\text{CN})_4$  ion in the spectra of the compounds under study, we refer to the vibrational data of  $\text{K}_2\text{Cd}(\text{CN})_4$  and  $\text{K}_2\text{Hg}(\text{CN})_4$  salts in the solid phase [29] (Table III). The structural studies of these salts have shown that the K-NC distance is ca.  $2.9\text{ \AA}$  in  $\text{K}_2\text{Cd}(\text{CN})_4$  [30] and  $\text{K}_2\text{Hg}(\text{CN})_4$  [31], while this bond length is ca.  $2.3\text{ \AA}$  in Td-type host frameworks [8, 9, 32]. Therefore, the spectral data of these salts may be used as references to account for the vibrational changes when the stiffer M-NC bonding takes place. The IR and Raman spectral data for  $\text{M}'(\text{CN})_4$  groups of our compounds studied are given in Table III, together with the vibrational data of  $\text{K}_2\text{Cd}(\text{CN})_4$  and  $\text{K}_2\text{Hg}(\text{CN})_4$ .

The assigned wavenumbers for the  $\text{M}'(\text{CN})_4$  group in the clathrates and the host complexes appear to be much higher than those of the units in  $\text{K}_2\text{Cd}(\text{CN})_4$  and  $\text{K}_2\text{Hg}(\text{CN})_4$  (Table III). Such frequency shifts have been observed for other Td-type clathrates [6, 7], and Td-type host complexes [8], in which both ends of



the CN group are coordinated, and explained as the mechanical coupling of the internal modes of  $M'(CN)_4$  with the metal (Cd–NC) vibrations [6–8].

The preceding discussion considered together leads us to the conclusion that the clathrates  $Mn(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$  ( $M'=Cd$  or  $Hg$ ) are similar in structure to the Td-type clathrates  $Cd(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$  ( $M'=Cd$  or  $Hg$ ).

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